

stream 33 at one or more acid addition points 34. The reaction mixture side stream 33 is located between the first cleavage reaction product withdrawal point 26 and the first cleavage reactor feed point 32.

5   **[0064]** The acid catalyst is used in an amount of from about 0.005% to about 0.1% by weight based on the first cleavage reactor feed flow 32. Concentrated sulfuric acid and other suitable acid catalysts are commercially available from a variety of sources.

10   **[0065]** The first cleavage reaction product 40 is fed to a second cleavage reactor 38, preferably a once through plug flow reactor, to produce a second cleavage reaction mixture. The second cleavage reactor 38 is operated at second cleavage reaction conditions effective to produce a  
15   second cleavage reaction product 44. The first cleavage reaction product 44 preferably is heated to a second cleavage reaction temperature and maintained in the second cleavage reactor 38 for a second cleavage reaction residence time effective to perform one or more,  
20   preferably all of the following functions: cleave 95 wt.% or more of remaining hydroperoxides present in the first cleavage reaction product; convert 70 wt.% or more, preferably 75 wt.% or more, more preferably 85 wt.% or more of DMBA (if present) in the first cleavage reaction  
25   product to AMS; and, convert 70 wt.% or more, preferably 75 wt.% or more, more preferably 85 wt.% or more of EMBA (if present) in the first cleavage reaction product to AES and 2P2B. In this preferred embodiment, selectivity of conversion of DMBA to AMS and/or of EMBA to AES and 2P2B  
30   is maximized. Generally the second cleavage reaction residence time is from about 5 seconds to about 1 minute.

**[0066]** Suitably, the second cleavage reaction conditions comprise a second cleavage reaction temperature of from about 60 °C to about 130 °C, preferably from about 70 °C to  
35   about 120 °C. The second cleavage reaction conditions also comprise a second cleavage reaction pressure which, when combined with the second cleavage reaction temperature, is sufficient to maintain the second cleavage reaction

mixture in the liquid phase. At the foregoing temperatures, a pressure of about 30 psig or more is sufficient. The second cleavage reaction product 44 is withdrawn from the second cleavage reactor 38 and passed to additional stages for recovering the cleavage products.

5 [0067] Cleaving initially at low temperature increases the yield of AMS, AES, and 2P2B, and reduces the amount of s-butylbenzene and/or cumene required to co-produce a given amount of phenol and MEK and/or acetone. Conversion

10 efficiency is improved and the formation of non-recoverable by-products during cleavage is reduced.

[0068] Depending on the ratio of s-butylbenzene hydroperoxide to cumene hydroperoxide, the cleavage produces a second cleavage reaction product 44 with molar

15 acetone:phenol ratios from about 0.8:1 to about 0.23:1. Molar MEK:phenol ratios in the second cleavage reaction product 44 are from about 0.2:1 to about 0.77:1. In a most preferred embodiment, the acetone to phenol ratio in the second cleavage reaction product 44 varies from about

20 0.44:1 to about 0.25:1.

[0069] Reactions which occur at lower temperatures occur in the early cleavage stages, preferably in the first cleavage reaction, which occurs in the first cleavage reactor 15. About 95% to about 98% conversion of

25 hydroperoxides to phenol and MEK and/or acetone is achieved in the first cleavage reactor 15. Reactions which require higher temperatures occur in the later cleavage stages, preferably in the second cleavage reactor 38. The conversion of DMBA to AMS and EMBA to

30 AES and 2P2B require relatively high temperatures of from about 70 °C to about 130 °C and these reactions are postponed, preferably until the first cleavage reaction product 40 reaches the second cleavage reactor 38. At this point, little hydroperoxide remains to be cleaved.

35 The second cleavage reaction conditions can be optimized to maximize the conversion of DMBA to AMS and EMBA to AES and 2P2B.

[0070] In a preferred embodiment, the safety of the cleavage reaction is enhanced compared to other embodiments. By using a pipeline loop reactor as the first cleavage reactor 15, it is possible to make multiple exotherm measurements to verify that the reaction is being carried out properly and to control the amount of acid catalyst added to the first cleavage reaction mixture side stream 33. In typical boiling pot cleavage reactors, acid addition typically is controlled by the single exotherm measurement taken at the sulfuric acid addition point. The single exotherm measurement is made by pumping a small amount of the cleavage reactor mixture out of the reactor at the acid addition point and mixing that small amount of the cleavage reaction mixture with acid. The exotherm generated upon acid addition is measured for process control and to determine if a shutdown is required for safety purposes. If the reaction is running well, then the exotherm measured is moderate (typically 15 °C). If the reaction is running too fast, then no exotherm is measured. If the exotherm is large (about 25 °C or more), then the reaction is running too slowly. The risk of the reaction running too slowly is that a runaway reaction can occur when additional acid is added.

[0071] Plug flow reactors (PFR's) and plug flow reactors with recycle (PFRR's) are especially adaptable to multiple exotherm measurements. Controlling acid addition based on multiple exotherm measurements lowers the risk of adding too little or too much acid catalyst to the first cleavage reactor 15 due to an incorrect exotherm measurement by any one failed control system component, and essentially decouples safety components from control components.

[0072] In a preferred embodiment, the exotherm preferably is measured across multiple locations. The exotherm is measured across one or more reaction mixture exotherm measurement points, preferably by measuring the temperature increase from measurement point 52 to measurement point 54 along the reaction mixture side stream 33. The exotherm also preferably is measured in

the first cleavage reactor 15 across one or more first cleavage reactor (FCR) exotherm measurement points, preferably by measuring the temperature increase from measurement point 35 to measurement point 37 along the first cleavage reactor 15. The exotherm also preferably is measured across the second cleavage reactor, preferably by measuring the temperature rise from measurement point 48 to measurement point 41. The exotherm may be measured using any suitable apparatus, such as thermocouples.

5     **[0073]** The second cleavage reaction product 44 is cooled, preferably via a heat exchanger 50, and fed to a neutralization apparatus (not shown) where the second cleavage reaction product 44 is subjected to neutralization conditions comprising a neutralizing base effective to produce a neutralized second cleavage reaction product. The neutralization conditions comprise a temperature of from about 40 °C to about 60 °C, preferably from about 45 °C to about 50 °C, and a pressure sufficient to maintain the second cleavage reaction product in the liquid phase. Atmospheric pressure or higher is sufficient for this purpose. The neutralization apparatus ensures thorough contact of the second cleavage reaction product with the base. Suitable neutralization apparatuses include, but are not necessarily limited to a vessel equipped with a stirrer and a pipe mixer.

10     **[0074]** Any suitable neutralizing base may be used. Preferred neutralizing bases are alkali bases. Suitable alkali bases include, but are not necessarily limited to hydroxides, carbonates, bicarbonates, and phenates of sodium, potassium, and lithium, and combinations thereof. The alkali base is used in an amount sufficient to maintain the neutralized aqueous fraction (described in the next paragraph) at a pH of from about 5 to about 11, preferably at a pH of from about 5 to about 5.5.

15     **[0075]** The neutralized second cleavage reaction product is separated into a neutralized organic fraction and a neutralized "aqueous" fraction. The weight ratio of the

neutralized organic fraction to the neutralized "aqueous" fraction suitably is from about 1:3 to about 3:1.

[0076] At least part of the neutralized "aqueous" fraction preferably is recirculated back to the neutralization apparatus. The remainder of the neutralized "aqueous" fraction may be discarded or recycled to some other part of the process. The salt concentration in the neutralized "aqueous" fraction increases over time, but preferably is maintained at from about 1 to about 30% by weight.

#### **Cleavage Product Separation Zone**

[0077] In a preferred embodiment, the cleavage product separation zone comprises a Crude Ketone Column (CKC). The neutralized organic fraction, or "CKC feed," is fed to the CKC 16 (Fig. 1) and exposed to CKC conditions effective to produce a bottom crude phenol fraction and a CKC vapor distillate.

[0078] The CKC conditions are effective to produce a CKC vapor distillate comprising most of the water (if present), cumene, s-butyl benzene, and AMS in the neutralized organic fraction. The CKC conditions preferably are effective to produce a CKC vapor distillate comprising 99 wt.% or more, preferably all of any water present in the neutralized organic fraction. The CKC conditions also preferably are effective to produce a CKC vapor distillate comprising 75% or more, preferably more than 75% of the hydroxy-ketones in the neutralized organic fraction. The CKC conditions also are effective to produce a crude phenol fraction comprising from about 2 wt.% to about 5 wt.% of a combination of cumene, s-butylbenzene, AMS, AES, and 2P2B.

[0079] In a preferred embodiment, the CKC conditions comprise a CKC top temperature of from about 190°C to about 220°C, preferably from about 203°C to 207°C, and a CKC top pressure of from about 0 psig to about 10 psig, preferably from about 3 psig to about 7 psig.

[0080] The crude phenol fraction is purified to a phenol product in a crude phenol refining zone 18 using known procedures.

5 [0081] The CKC vapor distillate is fed to a CKC vapor condenser and subjected to CKC vapor condenser conditions effective to produce a CKC vapor condensate. The CKC vapor condensate is separated into a CKC vapor condensate organic layer and a CKC vapor condensate aqueous layer. A portion of the CKC vapor condensate aqueous layer--  
10 called the "CKC recycle portion"--is fed to the CKC column at a recycle point. Although it is possible for the recycle point to be at a variety of locations on the CKC column, the recycle point most preferably is the same tray at which the neutralized organic fraction is fed to  
15 the CKC column. The CKC recycle portion comprises from about 50 wt.% to 95 wt.%, preferably about 75 wt.% to about 80 wt.% of the CKC vapor aqueous layer. The remainder of the CKC vapor condensate aqueous layer and  
20 the CKC vapor condensate organic layer are mixed to form a CKC vapor condensate mixture comprising 2 wt.% phenol or less, preferably 1wt.% phenol or less. The CKC minimum mass reflux ratio to effect this degree of phenol separation is about 0.05/1. In a preferred embodiment, the CKC conditions comprise a mass reflux ratio of from  
25 about 0.1/1 to about 0.2/1.

#### **MEK Recovery Zone**

[0082] MEK product and (if present) acetone are recovered in the MEK recovery zone 20 (Fig. 1).

#### **-Where cumene is not fed to the reaction mixture**

30 [0083] Where cumene is not fed to the oxidation reaction, the CKC vapor condensation mixture does not comprise a significant acetone component and is treated to recover MEK product. In this case, the CKC vapor condensate mixture is mixed with an aqueous base, preferably an  
35 alkali base, more preferably a sodium containing base, in an amount and concentration effective to catalyze the condensation of aldehydes in the CKC vapor condensate mixture with MEK. The base is fed in sufficient quantity to react with phenol in the CKC vapor condensate mixture

to form a phenate, preferably sodium phenate. The resulting mixture, herein called an "MEK recovery mixture" is subjected to MEK separation conditions effective to separate a MEK product.

- 5   **[0084]** The MEK separation conditions preferably comprise cooling the MEK recovery mixture to a temperature of from about 35 °C to about 55 °C, preferably from about 40 °C to about 45 °C, to produce a cooled MEK recovery mixture. The cooled MEK recovery mixture is fed to a MEK recovery
- 10 mixture decanter where the cooled MEK recovery mixture is separated into a MEK decanter aqueous stream and a MEK decanter organic stream. The MEK decanter aqueous stream preferably is recycled to the cleavage neutralization apparatus. The MEK decanter organic stream comprises
- 15 MEK, hydrocarbon, other organic species, and any dissolved water. The MEK decanter organic stream is subjected to a minimum of two aqueous washes. The first wash comprises washing the MEK decanter organic stream with aqueous alkali base to remove trace phenol,
- 20 producing a first washed MEK decanter organic stream. **[0085]** The first washed MEK decanter organic stream is exposed to first washed MEK decanter organic stream separation conditions effective to produce a first washed MEK
- 25 decanter aqueous phase and a first washed MEK decanter organic phase. The first washed MEK decanter organic phase is subjected to a second wash with water to remove trace alkali base, producing a twice washed MEK decanter organic stream. The twice washed MEK decanter organic stream is again separated into a final MEK
- 30 decanter aqueous phase and a MDC feed comprising a final MEK decanter organic phase. **[0086]** The MDC-feed is fed to a distillation column, called a MEK Dehydration Column (or, a "MDC"). The MDC feed comprises MEK, hydrocarbon, water, and other organic
- 35 species. The MDC feed is subjected to MDC conditions effective to produce a MDC overhead comprising water and organic species having a boiling point sufficiently lower than MEK to be separated from the MEK, and a MDC bottoms

comprising MEK. Organic species having a boiling point sufficiently lower than MEK include, but are not necessarily limited to methanol and ethanol.

5   **[0087]** In a preferred embodiment, the MDC conditions comprise feeding an entrainer to the MDC to remove the water from the MDC feed with minimal loss of MEK in the MDC overhead. In a preferred embodiment, the entrainer is selected from the group consisting of hexane, cyclohexane, heptane, and combinations thereof. A most  
10 preferred entrainer is cyclohexane.

**[0088]** In addition to MEK, the MDC bottoms generally comprises hydrocarbon and other organic species having a boiling point which is the same as or greater than MEK. The boiling point of MEK is 79.6 °C .

15   **[0089]** The MDC conditions comprise a temperature and a pressure which vary relative to one another. For example, when the MDC pressure is from about 3 to about 10 psig, the MDC temperature is from about 75 °C to about 90 °C. In a preferred embodiment, the MDC pressure is from about  
20 6 to about 7 psig and the MDC temperature is from about 80 °C to about 85 °C.

**[0090]** The MDC conditions also comprise a MDC minimum molar reflux ratio, based on the reflux flow to the overhead water flow, of 5/1. In a preferred embodiment,  
25 the MDC molar reflux ratio is about 10/1 to about 20/1.

**[0091]** The MDC bottoms is fed to a MEK product column ("MPC") and subjected to MPC conditions effective to separate the MDC bottoms into a MPC bottoms and a MPC overhead comprising product MEK. In one embodiment, the  
30 MPC overhead is the product MEK. In a preferred embodiment, the MPC overhead comprises a MPC purge stream comprising some MEK. In this embodiment, the MPC purge stream is effective to purge organic species having a boiling point less than MEK from the MPC. In this  
35 embodiment, a substantially pure MEK product is withdrawn as a side draw. Where purging occurs, the MPC purge stream is recycled back to the first cleavage reactor to provide the benefits to cleavage previously described.



[0092] The MPC conditions comprise a temperature and a pressure which vary relative to one another. For example, when the MPC pressure is about 0 psig to about 10 psig, the MPC top temperature is from about 85 °C to about 101 °C. Preferably, when the MPC pressure is from about 4 psig to about 6 psig, the MPC top temperature is from about 92 °C to about 95 °C. The MPC conditions further comprise a MPC molar reflux ratio, based on reflux flow to product flow, of 0.15 or more, preferably more than 0.15. In a preferred embodiment, the MPC molar reflux ratio is about 1.

[0093] The MPC bottoms comprises hydrocarbons and other organic species having a boiling point higher than MEK. The MPC bottoms is subjected to standard post-treatment for analogous streams in a phenol/acetone process before being returned to the oxidation reactor(s).

**-Where cumene is fed to the oxidation reaction**

[0094] Where cumene is fed to the oxidation reaction, a crude acetone/MEK fraction is exposed to acetone/MEK separation conditions in the MEK recovery zone 20 (Fig. 1). In a preferred embodiment, the MEK recovery zone comprises an Acetone Product Column (APC), and the APC feed is the CKC vapor condensation mixture.

[0095] The APC feed generally comprises from about 14 wt.% to about 45 wt.% acetone, from about 46 wt.% to about 15 wt.% MEK, about 14 wt.% water (if present), and about 23 wt.% hydrocarbon, together with a variety of by products. In one embodiment, where the oxidation mixture comprises from about 15 wt.% cumene to about 30 wt.% cumene, the APC feed has the following composition:

APC Feed Composition Range ( $\pm$ indicates small variations about these means are possible)		
	Wt%	Wt%
Cumene in Oxidation Feed	15	30
Acetone	16 $\pm$	28 $\pm$
MEK	44 $\pm$	32 $\pm$
Water	14 $\pm$	14 $\pm$
Hydrocarbon (mostly s-butyl benzene)	23 $\pm$	23 $\pm$
Phenol	<2%	<2%
Other (Aldehydes, Hydroxy-ketones, MO, methanol, ethanol)	<0.5%	<0.5%

**[0096]** Product acetone is recovered from the APC column either as an APC overhead, or as an APC side draw. When product acetone is recovered as the APC overhead, the product acetone may be tainted with "light" organic species having a boiling point less than acetone. In a preferred embodiment, the APC overhead comprises a purge stream comprising some acetone. In this embodiment, the APC overhead purges the light organic species having a boiling point less than acetone in an APC overhead, and a substantially pure acetone product is withdrawn from the APC column as a side draw. In this embodiment, the APC overhead is sometimes referred to as an "APC purge stream" for convenience. The APC purge stream preferably is recycled to the first cleavage reactor to provide the benefits to cleavage previously described.

**[0097]** The APC conditions preferably comprise feeding an APC base to the APC column. The APC base preferably is an alkali base, most preferably an aqueous solution of alkali base, most preferably an aqueous solution of sodium hydroxide. The APC base is effective to catalyze the condensation of aldehydes in the APC feed with MEK and acetone to produce condensation products. The APC bottoms comprises the condensation reaction products. The APC base also is effective to react with phenol in the APC bottoms to form sodium phenate. Hence, in a

preferred embodiment, the APC conditions are effective to produce an APC bottoms comprising MEK, water, hydrocarbon, condensation reaction products, and sodium phenate, and combinations thereof.

5    **[0098]** The APC conditions comprise an APC pressure of from about 400 to about 500 mm Hg and an APC temperature of from about 30 °C to about 50 °C, preferably an APC pressure of about 450 mm Hg and an APC temperature of about 40 °C. The APC conditions also preferably comprise  
10 an APC minimum molar reflux ratio of about 12, calculated as rate of reflux flow to side draw product flow on a molar basis. In a preferred embodiment, the APC conditions comprise a molar reflux ratio of about 15 or greater.

15    **[0099]** The APC bottoms is subjected to MEK separation conditions effective to separate a MEK product. The MEK separation conditions preferably comprise cooling the APC bottoms to a temperature of from about 35 °C to about 55 °C, preferably from about 40 °C to about 45 °C to produce  
20 a cooled APC bottoms. The cooled APC bottoms is fed to an APC bottoms decanter where the cooled APC bottoms is separated into an APC decanter aqueous stream and an APC decanter organic stream. The APC decanter aqueous stream preferably is recycled to the cleavage neutralization  
25 apparatus. Like the MEK decanter organic stream, the APC decanter organic stream comprises MEK, hydrocarbon, other organic species, and any dissolved water. Also, like the MEK decanter organic stream, the APC decanter organic stream is subjected to a minimum of two aqueous washes.  
30 The first wash comprises washing the APC decanter organic stream with aqueous alkali base to remove trace phenol, producing a first washed APC decanter organic stream.  
      **[00100]** The first washed APC decanter organic stream is subjected to decanter separation conditions effective to  
35 produce a first washed APC decanter aqueous phase and a first washed APC decanter organic phase. The first washed APC decanter organic phase is subjected to a second wash with water to remove trace alkali base,

producing a twice washed APC decanter organic stream. The twice washed APC decanter organic stream is again separated into a final washed APC organic phase comprising the "MDC feed" and a final washed APC decanter aqueous phase.

[00101]The MDC feed comprises MEK, hydrocarbon, water, and other organic species. The MDC feed is fed to a distillation column, called a MEK Dehydration Column or "MDC" and subjected to MDC conditions effective to produce a MDC overhead comprising water and organic species having a boiling point sufficiently lower than MEK to be separated from the MEK, and a MDC bottoms comprising MEK. Organic species having a boiling point sufficiently lower than MEK include, but are not necessarily limited to methanol and ethanol.

[00102]In a preferred embodiment, the MDC conditions comprise feeding an entrainer to the MDC to remove the water from the MDC feed with minimal loss of MEK in the MDC overhead. In a preferred embodiment, the entrainer is selected from the group consisting of hexane, cyclohexane, heptane, and combinations thereof. A most preferred entrainer is cyclohexane.

[00103]In addition to MEK, the MDC bottoms generally comprises hydrocarbon and other organic species having a boiling point which is the same as or greater than MEK. The remaining procedures are the same as described in the corresponding sections under the heading "Where cumene is not fed to the reaction mixture," above.

[00104]The application will be better understood with reference to the following examples:

#### Example 1

[00105]Batch oxidations were performed to measure the effect of reaction temperature on conversion vs. time and selectivity. Hydrocarbon mixtures having a weight ratio of s-butyl benzene to cumene of 7 to 1 were oxidized using depleted air with 7 vol. % oxygen at atmospheric pressure. The results, presented in the following

Tables, were measured using gas chromatography. The Table 1A reflects results at 110 °C:

Table 1A

Temperature 110°C	Compositions in Weight %					
Time, hours	2	4	6	8	10	12
Cumene	11.99	11.83	11.46	10.95	10.33	9.96
s-BBenzene*	85.37	85.51	84.52	82.69	80.10	79.33
AP**	0.03	0.05	0.08	0.12	0.21	0.32
DMBA	0.14	0.15	0.17	0.19	0.22	0.27
EMBA	0.01	0.03	0.07	0.05	0.09	0.11
CHP***	0.75	0.96	1.28	1.62	2.25	2.69
sBBHP****	0.41	1.03	1.96	3.15	5.02	6.63
Unknowns	0.10	0.12	0.14	0.18	0.23	0.35

\*s-butylbenzene

\*\*acetophenone

\*\*\*cumene hydroperoxide

\*\*\*\*s-butylbenzene hydroperoxide

Table 1B reflects results at 125 °C.

Table 1B

Temperature 125°C	Compositions in Weight %					
Time, hours	1	2	3	4	5	6
Cumene	12.13	11.69	11.10	10.26	10.06	9.55
s-BBenzene	85.90	84.11	81.53	78.30	77.61	76.26
AP	0.06	0.12	0.24	0.49	0.60	0.96
DMBA	0.11	0.14	0.19	0.29	0.34	0.46
EMBA	0.01	0.02	0.06	0.15	0.46	0.30
CHP	0.98	1.27	1.69	2.33	2.65	3.23
sBBHP	0.81	1.90	3.41	5.82	6.95	9.32
Unknowns	0.10	0.11	0.16	0.37	0.46	0.69

The foregoing results indicate that, when the reaction temperature was increased by 15 °C, the reaction time to achieve a given total hydroperoxide conversion was about halved.

### Example 2

[00106] A standard oxidation mixture was prepared containing 300 grams of sec-butyl benzene (sBB), and an amount of cumene effective to produce a weight ratio of sBB:cumene of 3.4:1. The oxidation mixture also contained 1% cumene hydroperoxide as an initiator. The oxidation mixture was exposed to oxidation conditions comprising a

temperature of 130 °C, an oxidizing agent comprising 500 cc/min. 7% O<sub>2</sub> in N<sub>2</sub>, and a steady pressure of 40 psig. All experiments were carried out in a 500 cc Buchi Type II reactor, with stirring rate of 1300 rpm.

5 [00107]The foregoing standard oxidation mixture was oxidized as a control to assess the effect of ammonia on the reaction. No ammonia or water was added to the control mixture. After 8 hours, the mixture contained 438 wppm formic acid, 860 wppm acetic acid, and 1510 wppm  
10 phenol.

[00108]In a first comparative experiment, during oxidation, gaseous NH<sub>3</sub> was bubbled through the standard oxidation mixture at a weight ratio of 9.2:1 based on the expected acid production, resulting in an ammonia feed  
15 rate of 3.26 cc/min.

[00109]In a second comparative experiment, 1.25 wt.% water was charged with the standard oxidation mixture. During oxidation, gaseous ammonia was bubbled through the oxidation mixture in an amount sufficient to neutralize  
20 73% of the expected acid production (molar ratio of NH<sub>3</sub> of 0.73:1 based on the expected acid production), resulting in feed rate of ammonia of 0.26 cc/min.

[00110]Measurements of cumene hydroperoxide (CHP), s-butylbenzene hydroperoxide (sBBHP), acetophenone (AP),  
25 DMBA, and EMBA were performed on samples taken every two hours from the control mixture, and every hour from the comparative experimental mixtures, with the following results:

**Table 2a Oxidation without NH<sub>3</sub>**

Time (hour)	1	2	4	6	8
CHP	2.3	3.1	5.2	7.0	7.7
sBBHP	1.3	3.5	7.1	10.3	12.1
AP	0.1	0.3	0.8	1.7	3.1
DMBA	0.3	0.3	0.7	1.3	2.3
EMBA	0.1	0.1	0.2	0.6	1.2

**Table 2b Oxidation with NH<sub>3</sub>  
with 9.2 : 1 NH<sub>3</sub> to expected acid amount  
Ammonia feed rate = 3.26 cc/min**

Time (hour)	1	2	3	4	5	6	7	8
CHP	2.0	3.1	4.4	5.5	6.4	7.0	7.5	7.6
sBBHP	1.8	3.7	5.9	7.8	9.5	11.0	12.1	12.7
AP	0.1	0.3	0.5	0.8	1.2	1.8	2.6	3.5
DMBA	0.2	0.3	0.5	0.6	0.9	1.3	1.8	2.4
EMBA	0.0	0.1	0.1	0.2	0.4	0.6	0.9	1.3

**Table 2c Oxidation with 1.25%  
H<sub>2</sub>O and NH<sub>3</sub> at 0.73 : 1 NH<sub>3</sub> to  
expected acid amount  
Ammonia feed rate = 0.26 cc/min**

Time (hour)	1	2	3	4	5	6	7	8
CHP	2.1	3.2	4.5	5.6	6.6	7.4	8.1	8.5
sBBHP	2.0	3.7	5.8	7.8	9.7	11.4	12.9	14.0
AP	0.1	0.3	0.5	0.8	1.2	1.8	2.6	3.4
DMBA	0.2	0.3	0.4	0.6	0.9	1.3	1.8	2.3
EMBA	0.0	0.1	0.1	0.2	0.4	0.6	0.9	1.2

The improvements are summarized in the following Table,  
and illustrated in Fig. 3:

**5 Summary of improvement as a result of NH<sub>3</sub> addition:**

**Compare**  
**w/ no NH<sub>3</sub>** (DMBA +  
**base case HP yield AP\* EMBA)\* Phenol**

NH<sub>3</sub>:acids  
= 9.2 :1,  
no water +2.3% -7.70% -12.4% -32.9%  
NH<sub>3</sub>:acids  
= 0.73  
:1, w/  
1.25%  
water +13.5% -35.70% -37.2% -73.4%

\* measured at total hydroperoxide  
level of 19.82%

5       **[00111]**After 8 hours, the hydroperoxide yield in the  
oxidation mixture charged with ammonia was 13.5% higher  
than in the control and phenol poison was 44% lower than  
10   in the control. After each oxidation mixture had reached  
20 w% hydroperoxides, the ammonia-charged oxidation  
mixture exhibited an AP production 36% lower than in the  
control and DMBA and EMBA were 37% lower than in the  
control. The results are graphically depicted in Figures  
10   3-5. Note that Fig. 3 also includes the results when dry  
NH<sub>3</sub> was added at a ratio of 330:1 based on expected acid  
production. In this experiment, AP was higher than in  
the control.

15       **[00112]**Persons of ordinary skill in the art will recognize  
that many modifications may be made to the foregoing  
without departing from the spirit and scope thereof. The  
embodiment described herein is meant to be illustrative  
only and should not be taken as limiting the invention,  
which is defined in the following claims.

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